

1.033.362



# PATENT SPECIFICATION

DRAWINGS ATTACHED

1.033.362

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## COMPLETE SPECIFICATION

### Improved Activated Fuel Cell Electrodes and Methods for their Activation

We, LEESONA CORPORATION, a corporation organized in the State of Massachusetts, United States of America, of 333 Strawberry Field Road, Warwick, Rhode Island, United

5 States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to improved activated fuel cell electrodes, to the method of activation and to fuel cells employing said electrodes.

15 In the production of electricity directly from a fuel and oxidant, the basic problem encountered in obtaining an efficient system is essentially one of chemical kinetics. It is necessary to carry out the reaction of fuel and oxidant so that the portion of energy degraded into heat is as small as possible. At the same time, the reaction rates must be high enough to provide economically sufficient current output from a practical sized cell. The basic problem is rendered more critical since 20 it is necessary that the components of the cell be highly resistant to corrosion and remain substantially unvarying under the operating conditions of the cell.

25 Thus, although fuel cells were known at least as early as the 19th century when Davy and Grove attempted to carry out the electrochemical oxidation of fuels, it was not until recently that research on fuel cells received renewed vigour. The desire to obtain a high power output per unit weight was a principal factor in influencing efforts to make a commercially feasible fuel cell. Recent developments have now made it apparent that fuel cells are commercially feasible and are capable 30 of far surpassing the efficiency of a heat engine. However, in spite of the modern developments in fuel cell technology, the

known cells are not completely practical from a commercial standpoint and research is going forward in an effort to obtain improved electrodes, fuels, and electrolytes as well as improvements in the overall design of the fuel cell.

45 In regard to the electrode, the research has been largely in the direction of a structure which (1) will permit more accurate control of the reaction interface, (2) has high activity with commercially available fuels and (3) is relatively light in construction. In the early fuel cells, the electrodes were substantially homo-porous. Therefore, to regulate the three phase interface of solid, gas and electrolyte, it was necessary to control the pore size of the electrode, pressure differential of the gas and surface tension of the electrolyte. As a practical matter, however, it was impossible to obtain pores completely uniform in size, therefore, the cell was always operated with the smaller pores of the electrodes flooded with electrolyte due to capillary action or with gas bubbling through the larger pores unused. To a substantial extent, the advent of bi-porous electrode structures as proposed by Francis T. Bacon minimized the problem of controlling the reaction interface, since in 50 a bi-porous system, the large pores face the gas supply and the smaller pores face the electrolyte. The three phase interface occurs 55 substantially at the bi-porous wall.

60 Bi-porous electrodes, however, still possessed a number of disadvantages. For example, it is necessary to construct bi-porous structures from metal powders having carefully controlled and well defined grain size employing a process having a number of individual operations such as sintering, compacting, etc., thereby resulting in a very expensive electrode. In addition, in a hydrogen-oxygen system, 65 the oxidation of hydrogen at the three phase 70

75 80

interface results in the formation of water within the pore structure, presenting a serious removal problem. Again, the prior art electrodes required the use of substantially pure 5 hydrogen, since impurities in the gas will cause blocking of the pores, preventing diffusion of hydrogen to the reaction interface.

The introduction of electrodes constructed from non-porous palladium-silver alloy membranes was regarded with a high degree of enthusiasm. Such electrodes are light in weight, 10 permit the diffusion of hydrogen, but prevent the passage of inert gaseous impurities into the electrolyte and allow water formation only 15 on the electrolyte side of the membrane. These cells, therefore, have solved to a substantial extent, the problems encountered with both homo-porous and bi-porous electrode structures. However, at the preferred operating 20 temperatures, the electrodes are relatively inactive or easily become polarized. Therefore, in order for such hydrogen diffusion electrodes to be completely feasible from a commercial standpoint, it is necessary that the palladium-silver 25 alloy membrane be activated in order that a fuel cell employing such an anode will provide a sufficient electrical output at lower operating temperatures.

Accordingly, it is an object of the present 30 invention to provide an activated non-porous hydrogen diffusion palladium-silver alloy electrode, which will be reactive at practical operating temperatures.

It is another object of the invention to 35 provide a fuel cell electrode which will sustain high current densities at relatively low operating temperatures.

According to the instant invention, a fuel 40 cell electrode is constructed from a non-porous palladium-silver alloy membrane and thereafter the membrane is coated with a thin film of "black". The term "black" means palladium, platinum, rhodium, a mixture of 45 palladium and rhodium, platinum and rhodium or platinum and iridium deposited in a very finely divided form. However, electrodes coated with palladium black provide substantially superior performance in a fuel cell, in comparison to other blacks, particularly 50 when in contact with the fuel gas. Depending upon the type of electrolyte employed in the cell, platinum black may be advantageously selected to coat the surface facing the electrolyte. All of the resultant electrodes possess 55 excellent electro-chemical characteristics and are particularly useful in low temperature fuel cell systems. The performance characteristics of a given fuel cell system when employing the present activated electrodes is surprisingly 60 superior in comparison with prior art electrodes including unactivated non-porous hydrogen diffusion palladium-silver alloy electrodes.

A fuel cell employing electrodes constructed 65 according to the present invention is illustrated

diagrammatically in the accompanying drawing which shows a diagrammatic illustration of a fuel cell employing the features of the present invention.

In the drawing, electrode J is a non-porous 70 hydrogen diffusion palladium-silver alloy electrode activated with a thin film of "black", such as palladium black. Hydrogen is passed into fuel compartment H through inlet F and gaseous impurities are vented through outlet 75 G. The oxidizing electrode L can be any conventional oxidizing electrode known in the prior art, for example, a bi-porous nickel nickel oxide/air electrode which may be activated by a cobalt-nickel deposit. Air is 80 passed into the oxidizing compartment K through inlet D and vented through outlet E. Electrolyte C, for example, a 75% aqueous potassium hydroxide electrolyte, is contained 85 between electrodes J and L and serves as an ion transfer medium. If desired, the electrolyte can be circulated by suitable means through electrolyte inlet and outlet A and B. Electrical current is removed from the cell 90 through external circuit M.

As is apparent from the drawing, hydrogen 95 gas diffuses through the activated palladium-silver alloy membrane separating an electron from the hydrogen fuel and passing the proton into the electrolyte. The electron is drawn off and carried via external route M to the oxidizing electrode.

Since only hydrogen is diffused through 100 the activated non-porous palladium-silver alloy membrane, impure hydrogen gas containing carbon dioxide, carbon monoxide, water, methane ammonia, etc. can be used as the fuel. Pure hydrogen will diffuse through the membrane, and the gaseous impurities are 105 easily removed by suitable venting. The impurities being concentrated in the fuel compartment cannot contaminate the electrolyte. Thus, an electrode capable of using relatively impure hydrogen is an important feature of the instant invention. Additionally, since the reaction occurs substantially at the electrolyte face of the non-porous palladium-silver alloy membrane, the formation of water occurs only 110 in the electrolyte. Thus, no problem is encountered due to electrode flooding. Water can be removed from the electrolyte as necessary by circulation through a suitable evaporation unit.

It has been found that palladium-silver 115 alloy membranes are surprisingly superior to pure palladium both in mechanical and electrochemical properties. Thus, palladium membranes have a tendency to become brittle after long periods of exposure to hydrogen under operating fuel cell conditions. Palladium-silver alloy membranes on the other hand do not demonstrate brittleness even after prolonged periods of exposure to hydrogen at high temperatures. Additionally, diffusion of hydrogen through an activated palladium- 120 125 130

silver alloy electrode is superior, particularly at lower temperatures. Another important feature is the potential stability of an activated palladium-silver membrane fuel cell electrode 5 in comparison with an activated palladium electrode in a fuel cell system. Allcys containing from 5—45% by weight of silver have been demonstrated to produce good results with an alloy composed of 20—10 35% silver showing optimum fuel cell electrode properties. At times, it may be desirable to include minor amounts, that is, up to 5% of an additional metal for example gold, tellurium, iridium and rhodium in the 15 palladium-silver alloy. The thickness of the non-porous palladium-silver alloy membranes for use as the electrodes depends to a large extent upon the pressure differential to be applied across the membrane 20 and upon the rapidity of the diffusion desired. Diffusion of hydrogen gas through the activated membrane is proportional to the pressure differential across the electrode, structure and the membrane thickness. The minimum 25 thickness is immaterial as long as the membrane is structurally able to withstand the necessary pressure of the fuel cell. Thus, it may be desirable to use an extremely thin activated palladium-silver alloy membrane 30 and support the membrane by external means. The preferred range of thickness is from approximately 0.5 to 30 mils. The membranes can be fabricated as flat supported sheets or 35 in a tubular or corrugated construction. In many cases a tubular construction is preferred since the effective surface area of the electrode will be increased. Additionally, a tubular construction is ideal for bi-polar or multi-polar cells. 40 After the non-porous palladium-silver alloy membrane is fabricated, it is coated with a thin film of "black". The "black" can be palladium, platinum, palladium-rhodium or rhodium. However, as stated hereinbefore, palladium has outstanding electrochemical characteristics and is preferred. Additionally, palladium black has a greater tendency to adhere to the non-porous palladium-silver 45 membrane. The "blacks" employed are obtainable by known prior art means. For example, by electrolytically depositing the metal from a solution, such as palladium from a  $PdCl_2$  solution. The coating of non-porous palladium-silver 55 alloy membranes with the "black" is performed by a method known in the art, for example, by electro-deposition from an aqueous acid solution. Surprisingly superior results are however achieved, particularly in regard 60 to film adherence by the method described in Specification No. 1033365 (6361/65) divested herefrom, namely by pre-exposing the electrode structure to be plated to hydrogen before plating with palladium black. Improved fuel cell performance is noted with the deposition 65 of from 0.5 to 50 milligrams of black per square centimeter of electrode surface with the usual amount being no more than about 1—15 milligrams of black per square centimeter of surface due to economic considerations. From a practical standpoint, any amount of black can be applied by the method described in Specification No. 1033365 (6361/65), however, it may be necessary to subject the structure to be plated to a further cathodic treatment. 70 Depending upon the ultimate use of the activated structures, it can be desirable to coat one surface of a non-porous structure with one thickness of black and the second surface with a different thickness, or the second surface can be coated with a different material such as platinum. The coating of the separate surfaces with different blacks or with different thicknesses of the same black can be accomplished by exposing both surfaces of the structure to hydrogen and thereafter coating one side with one black and after completion coating the second surface. When this procedure is followed, there is a tendency for some of the hydrogen adsorbed by the electrode to be lost. Thus, it may be desirable to expose the surface to be plated to an additional cathodic treatment before plating the second surface. Depending upon the techniques employed, modifications in the structures are obtainable. 80 One method of obtaining a different coating on the separate surfaces to be plated is disclosed in Specification No. 1033365 (6361/65). 85 It may not be desirable on all occasions to plate both sides of the non-porous palladium-silver alloy membrane with a suitable black. Thus, in a given system, it may be desirable to coat only the surface of the non-porous palladium-silver membrane which fronts the fuel or hydrogen gas side of the cell. The surface facing the electrolyte can be in an unactivated state. However, preferably, both 90 surfaces are coated with a suitable "black" since electrode poisoning is more prevalent with an unactivated surface. The decision whether both surfaces should be plated is within the ability of one skilled in the art, depending upon the particular needs of a given fuel cell system. 95 100 105 110 115 120 125 130

The present activated hydrogen diffusion electrodes are operable in fuel cell systems within a fairly wide temperature range. However, for good hydrogen diffusion, it is desirable that the temperature of the system be in excess of  $25^{\circ}C$  and preferably not over  $350^{\circ}C$ , with the optimum temperature range being in the neighborhood of  $100-300^{\circ}C$ . The present cells can be operated with a variety of electrolytes including aqueous alkalies such as potassium hydroxide, sodium hydroxide, potassium carbonate, and the alkylamines. Acid electrolytes which may be employed include sulphuric and phosphoric

acid. If an acid electrolyte is selected, it can be advantageous to coat the surface fronting the electrolyte with platinum black due to its exceptional resistance to attack by acids. An outstanding feature of the electrodes of the present invention is that the formation of water occurs only in the electrolyte and not in the electrode structure. Thus, the water does not affect the hydrogen diffusion and can be conveniently removed from the electrolyte by suitable means. Consequently substantially any electrolyte can be employed as long as it is capable of transferring ions and remains substantially invariant in a given fuel cell system.

Having described the invention in general terms, the following examples are set forth to more particularly illustrate the invention.

20 An activated non-porous palladium-silver  
allyc membrane prepared as described in  
Example 1 of Specification No. 1033365  
(6361/65), was compared with an identical  
structure which was unactivated. The com-  
parisons were carried out at 200°C. employ-  
ing 10 p.s.i.g. of hydrogen. The unactivated  
electrode at 82 millivolts polarization drew  
22 mA/cm<sup>2</sup> current whereas the activated  
electrode at 82 millivolts polarization drew  
696 mA/cm<sup>2</sup> current.

30 The activated palladium-silver alloy electrode structure was employed as the anode in a fuel cell system constructed substantially as that illustrated in the drawing. The cathode L was a cobalt-nickel activated bi-porous nickel electrode, described in Specification No. 1014587 (680/63). The electrolyte C was a 75% aqueous potassium hydroxide solution. The operating temperature was 200°C. Impure hydrogen was fed into fuel compartment H through inlet F at 10 p.s.i.g. and vented through outlet G. Air was fed into inlet D and vented through outlet E. The cell at .945 volts, including 50 milivolts electrolyte IR drop, drew a current of 150 mA/cm<sup>2</sup>.

### EXAMPLE 1

A non-porous 75% palladium-25% silver alloy membrane  $1\frac{1}{2}$  mils thick and having a diameter of  $2\frac{1}{2}$  inches was plated with a palladium black film. The reduction in  $PdCl_2$  was carried out for three minutes depositing approximately 2 milligrams palladium per square centimeter of palladium-silver alloy structure. The resultant electrode was compared with an unactivated structure at  $200^\circ C$ . employing 10 p.s.i.g. of hydrogen. The unactivated electrode at 82 millivolts polarization provided a current of  $37 \text{ mA/cm}^2$ , whereas the activated structure at 82 millivolts polarization provided a current of  $1.044 \text{ A/cm}^2$ .

### EXAMPLE 2

Employing the apparatus illustrated in Figs. 2 and 3 of Specification No. 1033365 (6361/65) a 1.5 mil thick non-porous 75%

palladium-25% silver alloy membrane having a diameter of 2½ inches was coated on one surface depositing 11.4 milligrams palladium black per square centimeter and the second surface plated with 4.9 milligrams palladium black per square centimeter. The structure as a half cell with side 1 fronting the gas and side 2 fronting the electrolyte at 82 millivolts polarization provided 1.044 A/cm<sup>2</sup> current.

### EXAMPLE 3

Employing the apparatus illustrated in Figs. 2 and 3 of the drawing of Specification No. 1033365 (6361/65), a 1.5 mil thick non-porous palladium-silver alloy membrane 24 inches in diameter was coated on one surface depositing 6.3 milligrams of palladium black per square centimeter and the second surface plated with 7.0 milligrams of platinum black per square centimeter. The structure as a half cell, with the side coated with palladium black fronting the fuel gas and the side coated with platinum black facing the electrolyte, at 82 millivolts polarization provided  $415 \text{ mA/cm}^2$  current.

In Examples 1-3, the non-porous palladium-silver alloy membrane was composed of 25 parts silver and 75 parts palladium. However, the alloy can be replaced by other alloys containing from about 5-45 parts silver.

Additionally, in Examples 1-3, the palladium black can be replaced by platinum black, rhodium black, palladium-rhodium black, platinum-rhodium black and platinum-iridium black.

## WHAT WE CLAIM IS:—

1. As a fuel cell electrode a non-porous palladium-silver alloy hydrogen diffusion electrode coated on at least one surface with a thin film of "black" as herein defined. 105
2. The electrode of claim 1 wherein the black is palladium black.
3. The electrode of claim 1 wherein the alloy is composed of from 20-35% silver and the remainder palladium. 110
4. In a fuel cell for the generation of electricity comprising at least one fuel electrode and at least one oxidizing electrode in contact with an electrolyte, the improvement wherein the fuel electrode is a non-porous palladium-silver alloy membrane coated on at least one surface with a thin film of "black" as herein defined. 115
5. The fuel cell of claim 4 wherein the black is palladium black. 120
6. The fuel cell of claim 4 wherein the alloy is composed of from 5-40% silver and the remainder palladium.
7. The fuel cell of claim 4 wherein the alloy is composed of from 20-35% palladium. 125
8. A fuel cell for the generation of electricity comprising a non-porous palladium-silver alloy membrane coated on at least the

surface fronting the fuel gas with a thin film of palladium black as the anode, a bi-porous cathode and an alkaline electrolyte.

9. The fuel cell of claim 8 wherein the 5 bi-porous cathode is a cobalt-nickel activated bi-porous nickel electrode.

10. The fuel cell of claim 9 wherein the electrolyte is aqueous KOH.

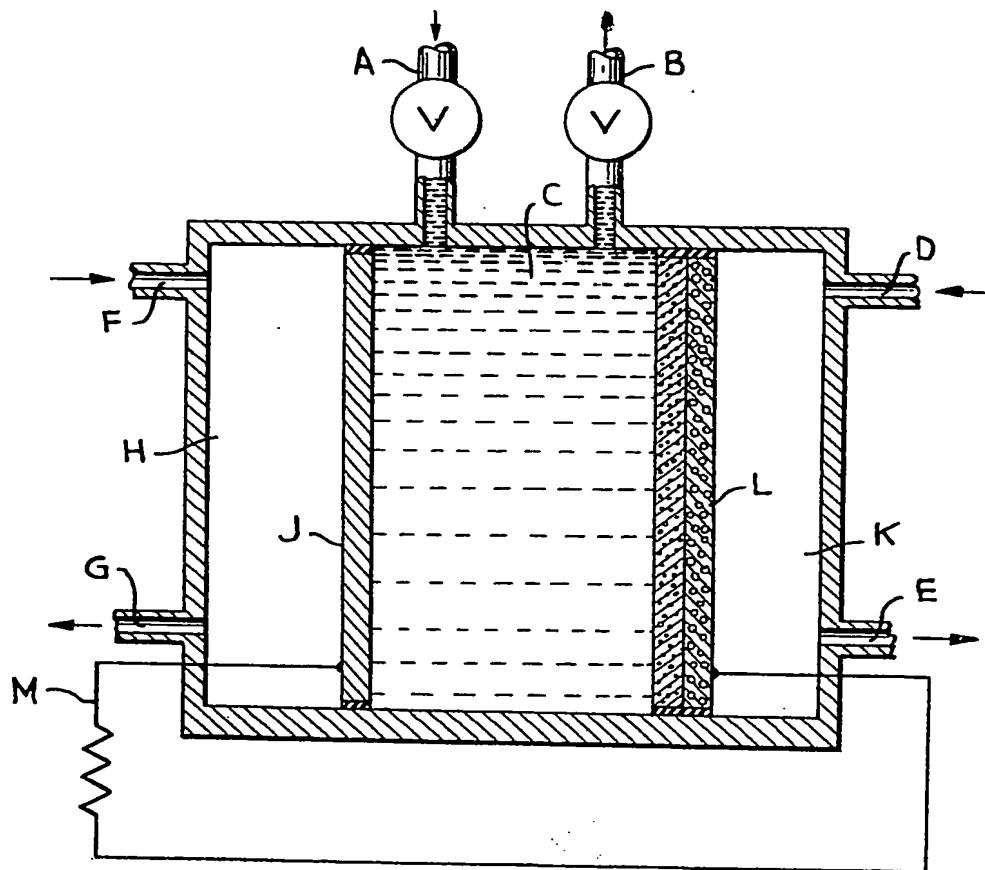
11. A fuel cell substantially as herein described with reference to the accompanying 10 drawing.

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1,033,362 COMPLETE SPECIFICATION  
1 SHEET  
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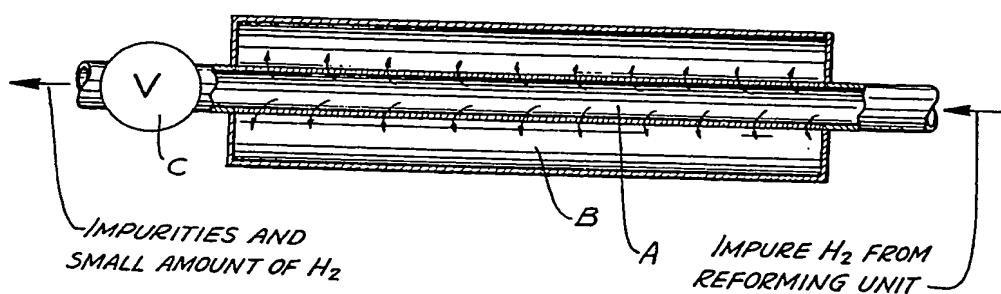
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3,148,089

HYDROGEN-PURIFICATION DEVICE FOR USE IN FUEL CELL

Filed Aug. 24, 1960

FIG. 1



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